



Stabilization and prolonged reactivity of aqueous-phase ozone with cyclodextrin

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ABSTRACT

Recalcitrant organic groundwater contaminants, such as 1,4-dioxane, may require strong oxidants for complete mineralization. However, their efficacy for in-situ chemical oxidation (ISCO) is limited by oxidant decay and reactivity. Hydroxypropyl-β-cyclodextrin (HPβCD) was examined for its ability to stabilize aqueous-phase ozone (O₃) and prolong oxidation potential through inclusion complex formation. Partial transformation of HPβCD by O₃ was observed. However, HPβCD proved to be sufficiently recalcitrant, because it was only partially degraded in the presence of O₃. The formation of a HPβCD:O₃ clathrate complex was observed, which stabilized decay of O₃. The presence of HPβCD increased the O₃ half-life linearly with increasing HPβCD:O₃ molar ratio. The O₃ half-life in solutions increased by as much as 40-fold relative to HPβCD-free O₃ solutions. Observed O₃ release from HPβCD and indigo oxidation confirmed that the formation of the inclusion complex is reversible. This proof-of-concept study demonstrates that HPβCD can complex O₃ while preserving its reactivity. These results suggest that the use of clathrate stabilizers, such as HPβCD, can support the development of a facilitated-transport enabled ISCO for the O₃ treatment of groundwater contaminated with recalcitrant compounds.

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1. Introduction

Groundwater contamination with recalcitrant, anthropogenic, organic chemicals remains a common and significant risk to human-health and water-resource sustainability. These contaminants may be treated using in-situ chemical oxidation (ISCO), which involves the introduction of oxidants into the subsurface where contaminants are transformed, through oxidation, into benign by-products (e.g., Huling and Pivetz, 2006). However, some organic contaminants (e.g., 1,4-dioxane) may require strong oxidants (i.e., compounds that have a standard redox potential greater than two volts) to be completely mineralized (Huling and Pivetz, 2006). Such contaminants are currently remediated using ex situ chemical oxidation (Zenker et al., 2003). This does require extraction of contaminated groundwater to the surface before treatment, which is generally inefficient and costly. Although advanced oxidation would be the preferred ISCO remediation method for recalcitrant contaminants, there are significant limitations in the use of strong oxidants for in-situ treatment.

Because of its relatively high standard oxidation potential (2.07 V), ozone (O₃) is a proven ISCO reagent for contaminated soil and groundwater (Bhuyan and Latin, 2012; Clayton et al., 2011; Huling and Pivetz,

2006). However, a key limitation for implementation of O₃, and other strong oxidants, in the treatment of recalcitrant contaminants is the short half-life and high reactivity of the oxidant in the subsurface environment (Huling and Pivetz, 2006). Radical scavengers, such as transition metals and soil organic matter associated with the subsurface materials, both aqueous and solid, can impose a significant oxidant demand, which ultimately reduces the amount of oxidant available for reaction with contaminants and increases the cost of treatment (e.g., Brusseau et al., 2011; Crimi and Siegrist, 2003; Marble et al., 2010; Mumford et al., 2004; Urynowicz, 2008; Xu and Thomson, 2009). The oxidant demand, as well as the reactivity of the oxidants, provides a serious challenge for the development of ISCO in general, and the variability and potential controls of O₃ oxidant demand in ISCO systems remains subject to research (e.g., Clayton et al., 2011; Huling and Pivetz, 2006; Lim et al., 2002; Masten, 1991; Masten and Davies, 1997; Wang et al., 2012).

O₃ is only sparingly soluble (~208 μM or 10 mg/L) in typical groundwater systems, and for that reason has mainly been injected as a gas (Masten and Davies, 1997). The half-life for aqueous O₃ is typically < 1 h due to the reactivity of the hydroxyl radical (OH•). This severely limits O₃ delivery to contaminants residing at significant distances away from the oxidant injection point. O₃ transforms contaminants through either direct oxidation or through decomposition and production of hydroxyl radicals, which then react with contaminants. Clayton

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et al. review the relatively selective direct O_3 :contaminant reaction mechanisms and indirect contaminant oxidation by radicals generated by O_3 (Clayton et al., 2011). The reactions that produce radicals from O_3 are generally thought to follow either the Hoigne, Staehelin, and Bader model (Hoigne and Bader, 1983a; Hoigne and Bader, 1983b; Hoigne et al., 1985) or the Tomiyasu, Fukutomi, and Gordan model (Tomiyasu et al., 1985) mechanisms (Clayton et al., 2011). Although, indirect oxidation using radical formation is highly reactive, this pathway may be limited in the presence of radical scavengers.

Use of oxidant stabilizers has been considered for increased oxidant stability and transportability within the subsurface (Huling and Pivetz, 2006). Oxidant stabilization generally involves addition of a chemical that forms a complex with an oxidant, which limits oxidant reactivity. Stabilizers have been developed mainly for iron (i.e., chelators) and hydrogen peroxide (H_2O_2) (i.e., phosphates or organic acids) (Watts et al., 2007). These modified-Fenton reaction methods then utilize a facilitated-transport approach to deliver the oxidant to the organic contaminants (Lee and Lee, 2010; Lewis et al., 2009; Lindsey et al., 2003; Wang and Brusseau, 1998).

Clathrates such as cyclodextrins have been shown to enhance the solubility and transport of both organics and metals (e.g., Blanford et al., 2014; Boving and McCray, 2000; Boving et al., 1999; Brusseau et al., 1994; Brusseau et al., 1997; Carroll and Brusseau, 2009; Chatain et al., 2004; Fourmentin et al., 2007; Gao et al., 2013; McCray et al., 2000; Skold et al., 2007; Tick et al., 2003; Wang and Brusseau, 1995). Cyclodextrins have also been used to complex iron, preventing the consumption of H_2O_2 and precipitation of iron (Lindsey et al., 2003). A ternary complex between the specific cyclodextrin called hydroxypropyl- β -cyclodextrin (HP β CD), Fe^{2+} , and pollutants has been observed (Liang et al., 2007). Veignie et al. demonstrated that certain cyclodextrins increase contaminant solubility while simultaneously supporting their degradation by Fenton's reaction (Veignie et al., 2009). It has been hypothesized that the formation of a ternary complex (i.e., pollutant-cyclodextrin-iron) enhances contaminant degradation by increasing the proximity of the contaminant to the OH^\bullet radical (Lindsey et al., 2003; Veignie et al., 2009).

O_3 is relatively hydrophobic, and could potentially be attracted to the hydrophobic cavity of HP β CD. The oxidative transformation of glucose with O_3 is well known (Marcq et al., 2009), and therefore destruction of HP β CD (i.e., a ring of glucose molecules) would be expected. However, HP β CD is generally more recalcitrant than the glucose building blocks, e.g. they are resistant to biological decay for a period of at least a few months (Wang et al., 1998). Prior work has not examined the potential for O_3 or other strong oxidants to oxidize HP β CD. Thus, it is currently unknown if and to what extent O_3 can degrade HP β CD and what transformation products are formed in the process. Examination of the potential for O_3 to transform HP β CD and/or for HP β CD to form a complex with O_3 is examined herein.

It is hypothesized that aqueous-phase O_3 partitions into the cavity of the HP β CD molecule, and that the formation of a HP β CD: O_3 inclusion complex (i.e., one chemical compound forms a cavity in which molecules of a second "guest" compound are located) prolongs the reactivity of O_3 in groundwater solutions. The objective of this research was to examine the potential for complexation of O_3 by HP β CD, as suggested previously (Ball, 2011), and the resulting impact on the stabilization and prolonged reactivity of the O_3 . Because HP β CD is a cyclic sugar,

consisting of glucose molecules, it must be expected that the HP β CD molecule is susceptible to oxidation. Therefore, the potential for O_3 to transform HP β CD was studied in aqueous-phase batch experiments. The ultimate goal was to provide insights into O_3 complexation by HP β CD and related facilitated transport processes that potentially extends the reactive lifetime and lateral reach of O_3 in subsurface environments. Such a technology could support ISCO remediation of groundwater contaminated with recalcitrant compounds.

2. Materials and methods

2.1. Materials

Hydroxypropyl- β -cyclodextrin, or HP β CD, (90% purity technical grade; average molecular weight: 1375 g mol^{-1}) was purchased from Sigma-Aldrich (Milwaukee, WI. Lot #BCBK6962V). A Barnstead NANOpure II (Series 550, Dubuque, Iowa) system was used to purify water used for all solutions to $>18 \text{ M}\Omega\text{-cm}$ (termed DI). A synthetic groundwater solution (Table 1) containing 9 mg/L $Ca(NO_3)_2$, 85 mg/L $CaCl_2$, 124 mg/L $MgSO_4$, 171 mg/L $NaHCO_3$, and 20 mg/L $NaCl$ prepared in DI was used for all experiments except when noted that DI was used. The synthetic groundwater represents the chemistry of the contaminated groundwater at Air Force Plant 44 (AFP44) in Tucson, Arizona, USA (Matthieu et al., 2013). All experiments were conducted at $20(\pm 1)^\circ\text{C}$. Gas-phase O_3 was generated using a G-series Pacific Ozone Generator (model #G1110101, Benicia, California), which was sparged through aqueous solutions to dissolve O_3 before each experiment.

2.2. Chemical analysis

Aqueous O_3 concentrations were determined by the indigo method (Bader and Hoigné, 1981) using a Milton Roy Spectronic 401 spectrophotometer, which has a reported precision to be 2% or $3 \mu\text{g/L}$ for O_3 analysis. Aqueous HP β CD samples were analyzed for concentration by fluorescence methods (Kondo et al., 1976) using a LS-55 Perkin Elmer spectrofluorometer. UV-Vis spectroscopy wavelength scans were also used to confirm HP β CD: O_3 complexation (SpectraMax M2, Molecular Devices). Additionally, HP β CD samples were analyzed for concentration and for identification of transformation products, by positive-ion electrospray ionization (ESI) Fourier transform ion cyclotron resonance (FT-ICR) mass spectrometry (MS), performed with a hybrid linear ion trap 7 T FT-ICR mass spectrometer (LTQ FT, Thermo, San Jose, CA). The mass spectrometer was equipped with a chip-based nano-electrospray ionization and sample-handling robot (Advion Triversa NanoMate) to produce positively- and negatively-charged ions. Prior to mass spectral analysis, samples were diluted 2-fold in methanol that contained 0.1% formic acid and $0.3 \mu\text{M}$ reserpine as an internal standard for signal normalization. Mass spectra were collected at a mass range of 300–2000 m/z and at mass resolving power of $m/\Delta m_{50\%} = 400,000$ (m/z 400). Internal mass calibration of FT-ICR mass spectra produces sub-part-per-million mass measurement accuracy, and enables the direct determination of elemental composition from measured mass to charge ratios. Thus, compounds were identified at the level of elemental composition based on accurate mass measurement by FT-ICR MS and linear ion trap mass spectra were used for relative quantitation. Peak lists generated from linear ion trap mass spectra were normalized to the internal

Table 1
Characteristics of synthetic groundwater used for all experiments.

Description	pH	TDS (mg/L)	Conductivity ($\mu\text{S/cm}$)	Eh (mV)
Synthetic groundwater	7.9	379	565	212
Hydrogeochemistry	Major cation	Concentration (mg/L)	Major anion	Concentration (mg/L)
	Na	54.7	Cl	66.5
	Ca	32.9	HCO_3^-	99.0
	Mg	25.0	SO_4^{2-}	124.0

standard signal by summation of all signals for doubly-charged HP β CD ions (singly-charged ions were not observed for all samples) and division by the internal standard signal intensity.

2.3. Ozone decay experiments

Batch, time-series experiments were conducted to measure the decay kinetics of O₃ in HP β CD solutions. For this, solutions were prepared spanning concentration ranges from 0 to 62.5 μ M (3.0 mg/L) O₃ and 2.2 to 727 μ M (3 mg/L to 1 g/L) HP β CD by mixing separate solutions each containing O₃ or HP β CD which were combined, mixture concentrations were measured, and mixed solutions were agitated for up to 70 h. All tests were conducted in triplicate, including two control experiments (i.e., no HP β CD), using synthetic groundwater and 125 mL amber VOA vials without headspace. The vials were sampled sacrificially at predetermined time intervals with a gastight syringe (Hamilton Company, Reno, Nevada), followed by immediate O₃ analysis by the indigo method. Results within the 95% confidence intervals are reported. The pH, temperature, and oxidation-reduction potential (ORP) were also measured. Samples collected at the end of these experiments and additional mixtures prepared at various HP β CD (5–500 mg/L; 3.64–364 μ M) and O₃ (0.5–2 mg/L; 10.4–41.6 μ M) concentrations were analyzed for HP β CD and transformation products.

2.4. Ozone stabilization experiments

The stabilization, longevity, and prolonged reactivity of O₃ in HP β CD solution was measured in batch, time-series experiments. The primary difference between these and the Section 2.3 O₃ decay experiments was that during the O₃ stabilization experiments indigo was present in the batch reactors and concentrations of indigo were monitored over time rather than O₃ concentrations. Equal volumes of freshly prepared O₃ and HP β CD solutions were mixed in 125 mL amber VOA vials containing 10 mL of a potassium indigo trisulfonate (without headspace). Control experiments were conducted to monitor the natural indigo decay in the absence of O₃. At predetermined times triplicate samples were collected and analyzed for indigo, the 95% confidence interval was calculated, and subsamples were monitored for pH, temperature, and ORP.

3. Results and Discussion

3.1. Ozone transformation of HP β CD

The potential for transformation of HP β CD by O₃ was examined using linear ion trap relative quantitation of HP β CD by broadband positive-ion ESI FT-ICR mass spectroscopy with and without O₃ exposure. Fig. 1 presents the resulting HP β CD relative concentration for various initial HP β CD concentrations, and experiments with identical HP β CD solution concentrations before and after exposure to O₃ are compared. Fig. 1A, B, and C contain results for HP β CD exposed to O₃ concentrations of 0.5 mg/L (10.4 μ M), 1 mg/L (20.8 μ M), and 2 mg/L (41.7 μ M), respectively. The HP β CD relative concentration was generally reduced relative to the result without O₃ exposure, which confirms that O₃ does react with HP β CD and the decreased HP β CD concentrations are due to transformation of HP β CD by O₃. However, only a fraction of HP β CD was transformed during this reaction.

Fig. 2 shows the percentage of HP β CD transformed as a function of the O₃:HP β CD molar ratio. The results indicate that when the O₃:HP β CD molar ratio was high (>2:1), as much as 76% of the HP β CD was transformed. At a molar ratio of approximately 1:1, about 60% of the HP β CD was transformed, whereas transformation was limited to 2 to 21% at a 1:~11 ratio. Importantly, above a O₃:HP β CD molar ratio of 2:1, the fraction of remaining HP β CD (~25%) remained constant, which suggests that this fraction of the HP β CD resisted ozonisation

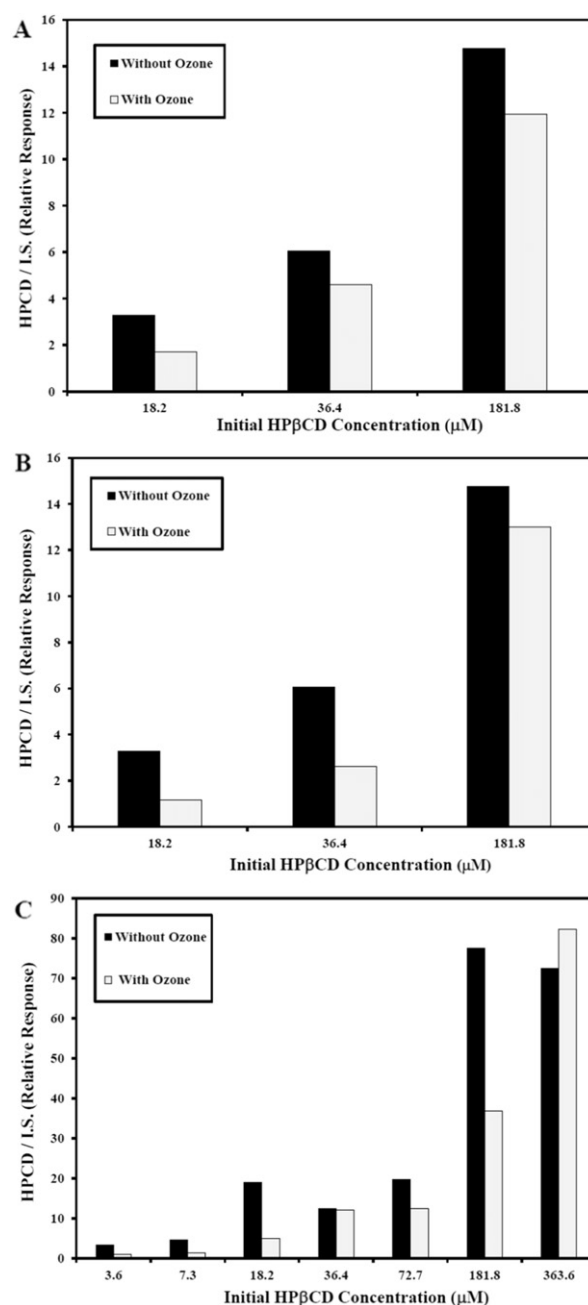


Fig. 1. Linear ion trap relative quantitation of HP β CD with and without (A) 0.5 (10.4 μ M), (B) 1 (20.8 μ M), and (C) 2 mg/L (41.7 μ M) ozone concentrations (LS = internal standard).

and apparently was stabilized, possibly by complexing O₃ inside its cavity.

The interaction of O₃ with HP β CD at the molecular level was also studied by broadband positive-ion ESI FT-ICR mass spectroscopy. The results for synthetic groundwater treated with 250 mg/L (181.8 μ M) HP β CD and 2 mg/L (41.7 μ M) O₃ are shown in Fig. 3a. A successive substitution of 2-hydroxypropyl groups (up to ten 2-hydroxypropyl groups per molecule) to singly- and doubly-charged HP β CD ions was observed. Sodium ([M + Na]⁺) was the predominant singly-charged ions adduct (Fig. 3b), whereas doubly-charged ions included calcium, magnesium, lithium, and potassium, as illustrated in Fig. 3c. The elemental composition assignments were confirmed by mass measurement with high-resolution FT-ICR MS, which was performed for the O₃-treated (i.e., with O₃) and control groundwater samples prepared with identical concentrations of HP β CD but without O₃. Further, negative-ion mode FT-

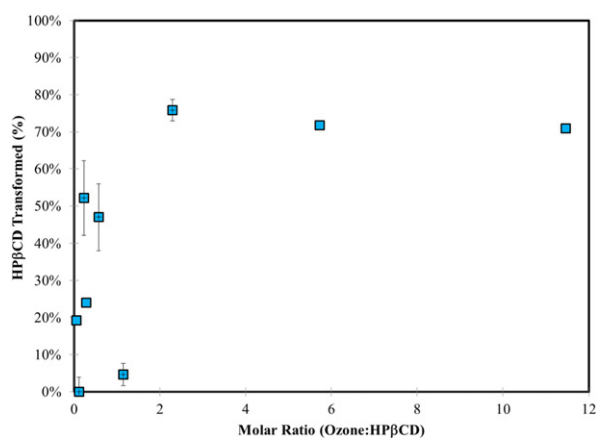


Fig. 2. Percentage of HPβCD transformed by ozone as a function of the Ozone:HPβCD molar ratio. Error bars represent the 95% confidence intervals.

ICR mass spectra were monitored for HPβCD reaction products (data not shown). The HPβCD concentration decreased, and each hydroxypropyl group decreased without observing the formation of reaction/oxidation products or removal of any one of the hydroxypropyl peaks (Fig. 3d). The sugars on HPβCD molecules have the acetal functional group which may have been cleaved by O_3 , which would result in cyclic esters and loss of chelating functionality. Together, the data indicate that ozonization mineralized (likely forming CO_2) up to 76% of the HPβCD but without completely eliminating the HPβCD ion signals (Fig. 2).

3.2. Ozone decay and stabilization within HPβCD inclusion complex

The fraction of HPβCD not mineralized by the O_3 formed an inclusion complex with the oxidant, and this likely shielded the HPβCD from further transformation while stabilizing the O_3 . Evidence for the formation of a HPβCD: O_3 complex was discovered as a shift in UV–Vis

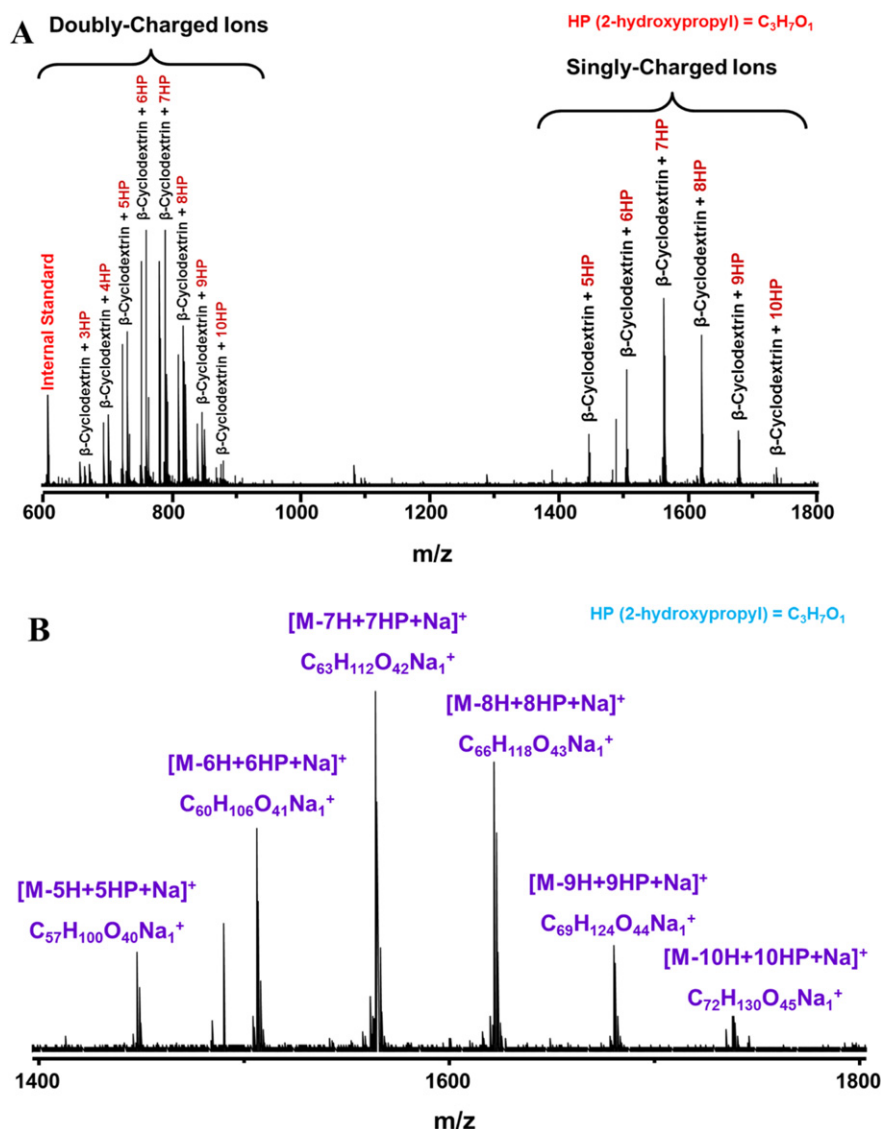


Fig. 3. (A) Broadband ESI FT-ICR MS for HPβCD (250 mg/L; 182 μM) in groundwater with 2 mg/L (41.7 μM) ozone. (B) FT-ICR MS (expanded from A) illustrating singly-charged ions (the observed sodium adducts ($[M + Na]^+$) show serial addition of 2-hydroxypropyl groups), and (C) doubly-charged ions. (D) Linear ion trap MS for HPβCD showing transformation of HPβCD (originally 250 mg/L; 182 μM) upon exposure to 2 mg/L (41.7 μM) ozone in groundwater by comparison of spectra with and without ozone exposure, peak heights are scaled to largest peak, and internal standard concentrations are identical.

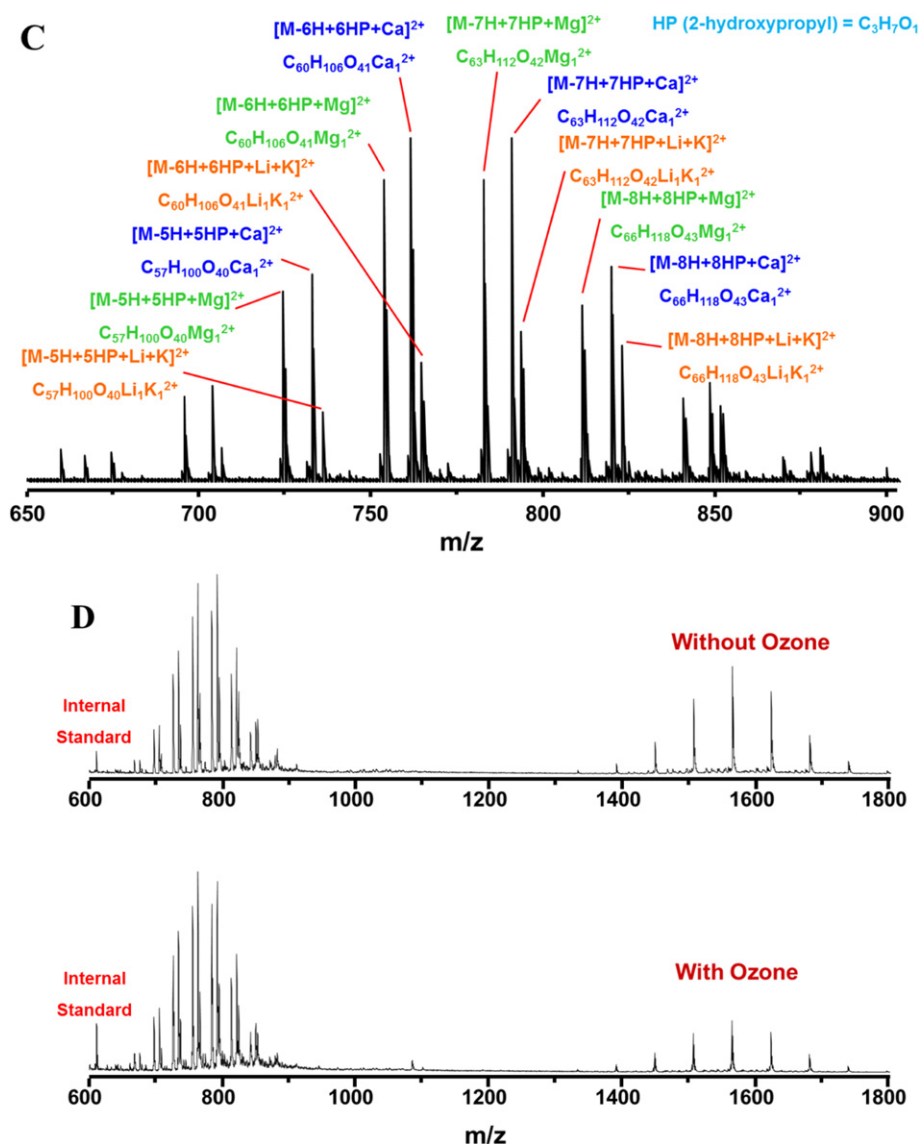


Fig. 3 (continued).

spectroscopy wavelength scan results for solutions containing HP β CD and O_3 within DI compared to unmixed solutions at identical concentrations. Shifts in spectroscopy absorbance have previously been used to

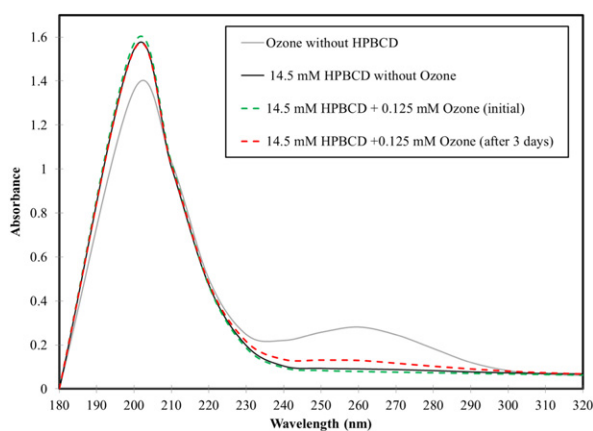


Fig. 4. Spectrophotometry confirmation of ozone complexation by HP β CD. HP β CD adsorbs at 205 nm, and absorbance increases at 205 nm with addition of ozone then decreases when ozone decays after 3 days. Ozone absorbance occurs at 205 nm and 260 nm.

identify aqueous complexation (e.g., Jung et al., 2013; Liang et al., 2007). Fig. 4 presents the absorbance data versus wavelength for solutions containing 20 g/L (14.5 mM) HP β CD with and without 6 mg/L (0.125 mM) O_3 . The spectrophotometric wavescan absorbance shifted for the HP β CD peak at 205 nm upon addition of O_3 . HP β CD adsorbs at 205 nm (O_3 adsorbs at 260 nm), and the absorbance at 205 nm increased with addition of O_3 compared to the scan without O_3 . After 3 days, the sample was reanalyzed and the peak at 205 nm had reduced absorbance relative to the scan after O_3 was added, and became comparable to the initial scan before the O_3 was added. The increase in

Table 2

Comparison of ozone concentration decay pseudo 1st order rate constants (k) and half-life times in synthetic groundwater solutions with varying HP β CD to O_3 mole ratios. " O_3 in groundwater" contains no HP β CD.

Description	k (hours $^{-1}$)	O_3 Half-Life (hours)
O_3 in DI water	0.49	1.40
O_3 in groundwater	1.89	0.37
O_3 in groundwater (repeat)	1.62	0.43
1:14.5 (HP β CD: O_3)	1.89	0.37
17.5:1 (HP β CD: O_3)	0.10	6.73
34.6:1 (HP β CD: O_3)	0.05	14.8

absorbance at the HP β CD wavelength upon O₃ addition suggests that O₃ and HP β CD form an inclusion complex, and this is confirmed by the isosbetic (wavelength crossover) point at 210 nm. Additionally, the reduction of the absorbance back to the level observed without O₃ addition, suggests that O₃ left the HP β CD cavity, and was decayed through reaction with aqueous hydroxide to form hydroxyl radicals over time. Based on the O₃ half-life in water (Table 2), the O₃ would have been completely degraded after the 3 days. These data confirm that the HP β CD:O₃ complexation forms, and is also reversible. The mechanism that is generally accepted for inclusion-complex formation within the HP β CD cavities is hydrophobic partitioning (Connors, 1997). Partitioning of O₃ into the HP β CD cavity can also be attributed to this mechanism, because of the hydrophobicity and low polarity of O₃. This is analogous to hydrophobic partitioning of low polarity compounds into surfactant micelles or to the surface of low polarity organic

matter, and this partitioning is generally considered to be a weak attraction force that is generally reversible.

O₃ decay was studied in DI water and synthetic groundwater with and without HP β CD. The decay followed pseudo 1st-order reaction kinetics in the synthetic groundwater with and without HP β CD (Fig. 5a and b). In HP β CD free groundwater, the dissolved O₃ half-life was 0.43–0.37 h ($k = 1.6$ – 1.9 h^{−1}) (Table 2), confirming literature values for groundwater/O₃ systems. In DI water, the O₃ half-life approximately tripled (1.4 h). The more rapid decay in the synthetic groundwater is attributed to the slightly basic pH (7.9) and the presence of salts, which may act as radical scavengers (e.g., Rużyło et al., 1998).

The half-life of O₃ in groundwater solutions with an overabundance of HP β CD increased to 6.73 h ($k = 0.103$ h^{−1} at HP β CD:O₃ mole ratios of 17.5:1) and 14.75 h ($k = 0.047$ h^{−1} at HP β CD:O₃ mole ratios of 34.6:1), respectively. The O₃ half-life and HP β CD:O₃ mole ratios were linearly

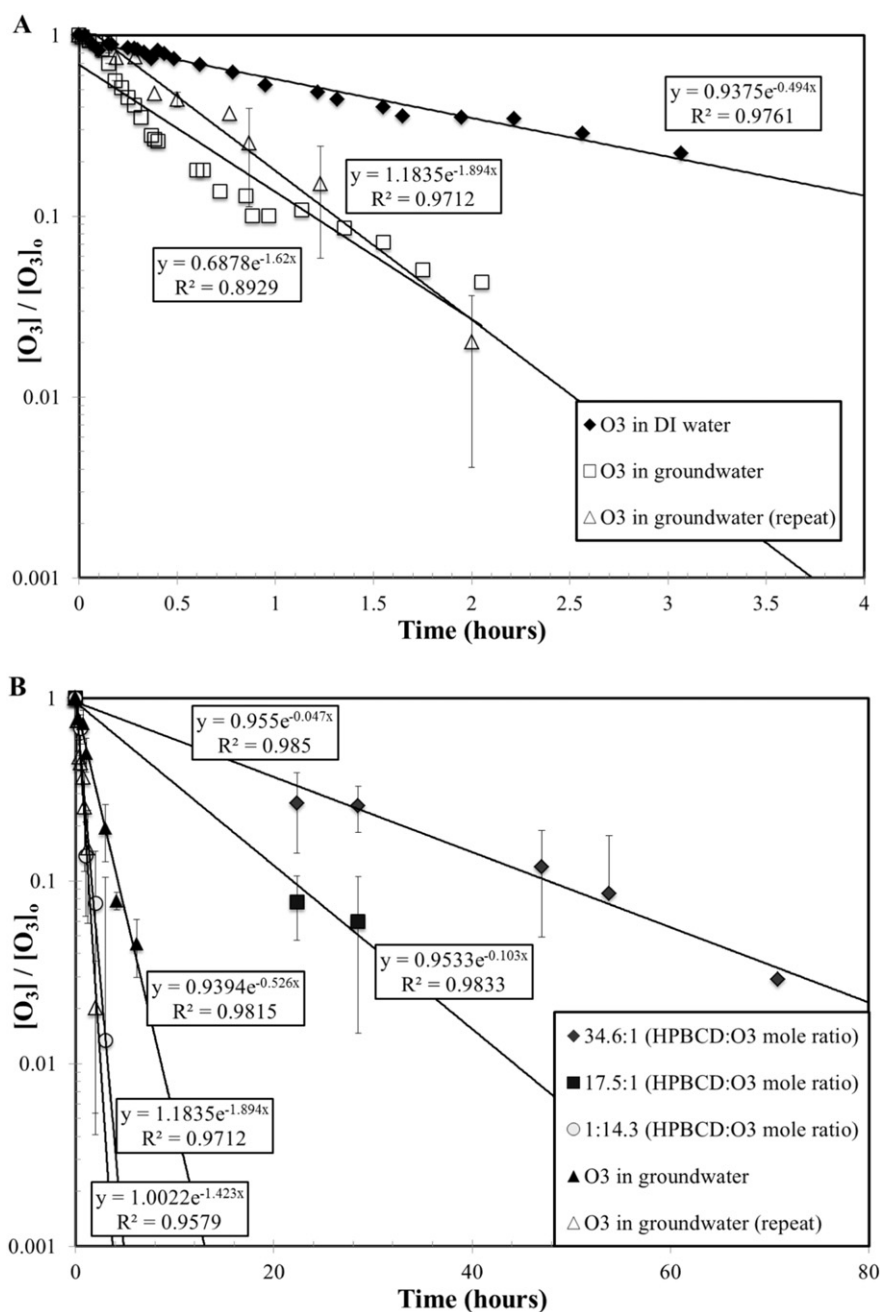


Fig. 5. (A) Ozone decay in DI and groundwater and (B) in groundwater containing varying HP β CD:O₃ molar ratios. Error bars represent the 95% confidence interval for triplicates. Pseudo 1st order kinetic analysis was used.

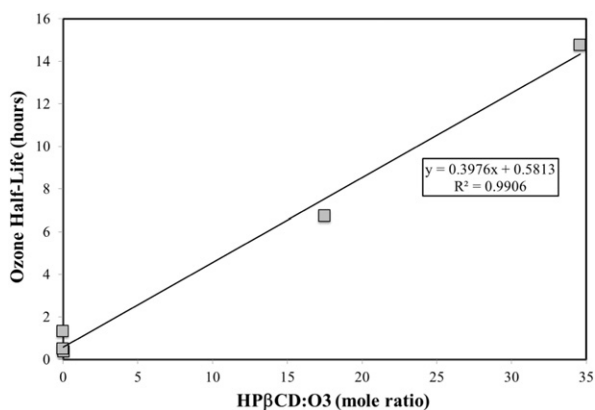


Fig. 6. Ozone half-life (ozone decay experiments; see Table 2) times plotted as a function of HPβCD:O₃ molar ratio, and the line presents the linear regression analysis.

related (Fig. 6). The addition of HPβCD to water does decrease the pH by 1 to 2 units and this alone can increase O₃ half-life. However, this effect was similar to, or less than, the half-life difference observed for DI water compared to groundwater, and cannot account for the half-life increase of up to a factor of ~40 observed with HPβCD.

3.3. Ozone stabilization and release from the HPβCD inclusion complex

The cumulative O₃ mass release from the HPβCD:O₃ complex and stabilization of the oxidant in aqueous phase was investigated with the indigo indicator in solution in a series of experiments with HPβCD:O₃ molar ratios ranging from 873:1 (20 g/L or 14.5 μM HPβCD with 0.8 mg/L or 0.017 μM O₃) to 10:1 (0.17 g/L or 0.12 μM HPβCD with 0.6 mg/L or 0.013 μM O₃). The compilation of results from these 9 experiments are summarized in Fig. 7, which displays the cumulative increase of free dissolved O₃ over time as indicated by continuous reaction with indigo (i.e., O₃ indicator and model contaminant). Control experiments (without O₃; data not shown) confirmed that indigo concentration did not change with HPβCD addition, i.e. there was no evidence for the removal of indigo through either decay or complexation with HPβCD.

These results show that for the duration of the experiments (>70 h), O₃ was continuously released from the HPβCD and that the O₃ remained reactive, as indicated by the destruction of the indigo throughout the experiment. This confirms that the formation of the HPβCD:O₃ inclusion complexation is a reversible process and, importantly, that the O₃ reactivity was conserved during the period of inclusion. For comparison, in aqueous solutions without HPβCD, O₃ is only reactive and measurable for ~5–6 h (i.e., ½ h half-life), and O₃ in solution with HPβCD had prolonged reactivity of over an order of magnitude (i.e., >70 h), which is comparable to results of the other batch O₃ decay experiments. The data also indicate that a large fraction of the O₃ initially present was released, and the fraction of released O₃ increased with increasing HPβCD:O₃ molar ratio. This finding has important implications for possible future application of this oxidant stabilization and delivery method.

Starting with a comparatively low initial O₃ concentration (e.g., 0.6 mg/L or 0.013 mM) the rate of O₃ release slowed down toward the end of the experiment. This indicates when using low initial O₃ concentrations a large fraction of the O₃ was lost, either due to decay within the HPβCD cavity or because of oxidative transformation of the HPβCD. However, reactivity did persist even in these experiments for ~70 h, which further supports that released O₃ would be available for reaction with contaminants as indicated by the observed indigo transformation. The results support the hypothesis that the partitioning of O₃ into the HPβCD cavity can, in fact, stabilize the reactivity of O₃ in groundwater solutions.

3.4. Implications for in-situ chemical oxidation of contaminated groundwater

This study demonstrates that the application of HPβCD to groundwater solutions containing O₃ can potentially enhance the oxidant lifespan and prolong oxidant reactivity for days and thereby can possibly improve the oxidant delivery farther away from the injection location. This would enhance the radius of influence of the ISCO treatment beyond what is currently possible when injecting aqueous O₃ into the subsurface. Co-injection of HPβCD with O₃ into groundwater would increase the O₃ transport distance by more than an order of magnitude, which could be applied as a source-treatment alternative, and it could be used to maintain a reactive flow-through treatment for groundwater

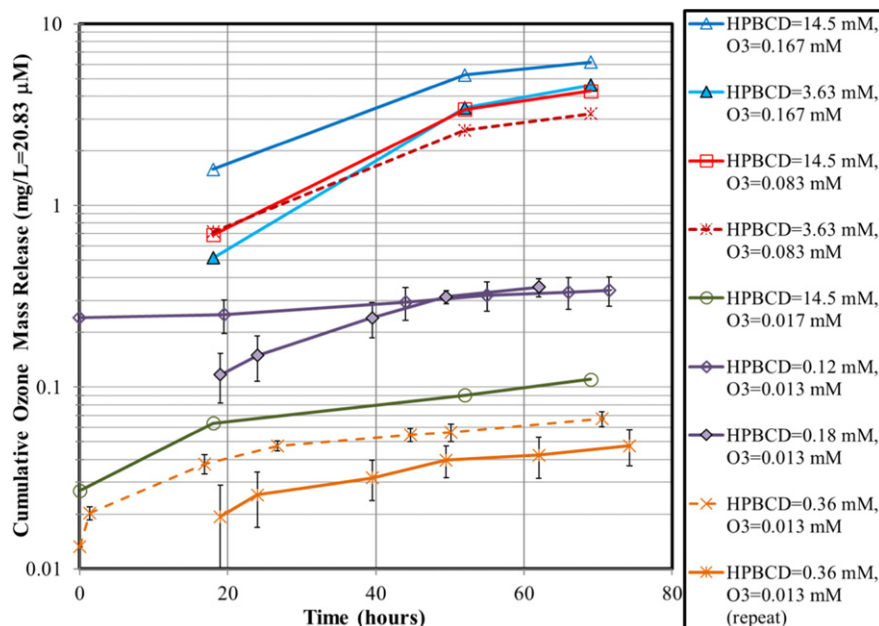


Fig. 7. Stabilized ozone cumulative concentration versus time with potassium indigo trisulfonate in HPβCD solution with various HPβCD to ozone ratios. Error bars (where present) represent the 95% confidence intervals.

contamination plumes. As H_2O_2 stabilization using organic-acid stabilizers has been demonstrated previously (Watts et al., 2007), this $HP\beta CD:O_3$ complex may also support ISCO using peroxide reactions.

The focus of this study was on aqueous reactions without adding further complexity of potential reactions between aqueous and solid mineral phases, which would need to be considered for implementation of ISCO treatment of groundwater contaminants. We acknowledge that the presence of organic matter, iron, manganese, and other redox-sensitive mineral phases in natural sediments might affect the lifetime of O_3 in the subsurface with and without the addition of cyclodextrins including $HP\beta CD$. Further investigation is ongoing that includes natural, metal oxide containing minerals. As noted previously, radical scavengers, such as transition metals and soil organic matter associated with the subsurface materials, both aqueous and solid, can impose a significant oxidant demand. However, oxidant stabilizers, such as a $HP\beta CD:O_3$ complex, may potentially inhibit reactivity of oxidants with reactive solid minerals by shielding a fraction of the oxidant within the $HP\beta CD$ cavity. Stabilization may also increase the potential for enhanced reaction selectivity. For the $HP\beta CD:O_3$ inclusion complex, nonpolar contaminants, such as chlorinated solvents, might compete with O_3 to occupy the $HP\beta CD$ cavity, which may potentially increase the selectivity of using O_3 for the oxidation of those types of contaminants.

4. Summary

The results of this investigation support the hypothesis that $HP\beta CD$ forms an inclusion complex with O_3 , and the partitioning of O_3 into the $HP\beta CD$ cavity can, in fact, stabilize and prolong the reactivity of O_3 in groundwater solutions. In particular, it was discovered that $HP\beta CD$ was only partially degraded by O_3 , and that a fraction of the $HP\beta CD$ formed a $HP\beta CD:O_3$ inclusion complex. This complex stabilized O_3 and increased the lifespan of O_3 in groundwater solutions containing $HP\beta CD$ by a factor of up to 40, relative to $HP\beta CD$ -free solutions. The O_3 half-life enhancement was linearly related to the $HP\beta CD:O_3$ molar ratio. Also, the formation of the inclusion complex was reversible, which stabilized O_3 and sustained indigo transformation (used herein as an indicator and model contaminant), and it prolonged O_3 reactivity. The results reported in this study have implications for development of facilitated-transport enabled ISCO using strong oxidants for the treatment of groundwater contaminated with various recalcitrant compounds including 1,4-dioxane. Although these results support our understanding of O_3 based ISCO, it is important to note that the laboratory-scale results presented herein may not directly translate to field-scale conditions.

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